

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE	3. REPORT TYPE AND DATES COVERED FINAL 01 Nov 91 TO 31 Jul 95	
4. TITLE AND SUBTITLE ANALYTICAL METHODS USING SLATER-TYPE ORBITALS IN QUANTUM CHEMISTRY			5. FUNDING NUMBERS F49620-92-J-0063 2300/HS 61102F	
6. AUTHOR(S) Prof. Herbert W. Jones			8. PERFORMING ORGANIZATION REPORT NUMBER AFOSR-TR-95 0791	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Dept of Physics Florida A&M University Tallahassee FL 32307				
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) AFOSR/NL 110 Duncan Ave Suite B115 Bolling AFB DC 20332-8080 Dr Michael R. Berman				
11. SUPPLEMENTARY NOTES 19960103 042				
12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited.			12b. DISTRIBUTION CODE DTIC QUALITY INSPECTED Approved for public release Distribution Unlimited	
13. ABSTRACT (Maximum 200 words) It has been our objective and that of several other groups to use Slater-type orbitals, STOs, characterized by $\exp(-R)$ in problems of ab initio quantum chemistry rather than the currently used Gaussian-type orbitals, GTOs, characterized by $\exp(-R^2)$. We believe that STOs will give more accurate results because they can fulfill a cusp condition and have correct asymptotic behavior. This was proven by us in the case of H_2 . But the real test would be for molecules with two or more atoms and electrons. The general molecular problem requires at most four-center molecular integrals. In just the last year devised an accuracy and fast method for processing STO molecular integrals: interior regions are done by Gauss-Legendre integration after A-function expansions, and exterior regions analytically with the aid of look-up tables for the evaluation of basic integrals. C, E, and F matrices that facilitate the calculations are stored in memory. All our procedures have been checked by the computer algebra program Mathematica, which can overcome all cancellation errors. The fact that several groups have worked many years on the STO integral problem without achieving the goal of a complete integral package, reveals the inherent difficulty of translating analytic formulation into computer programs. The most difficult part, namely, radial integrals, has now been solved with the support of the AFOSR.				
14. SUBJECT TERMS Now, it remains to use this strategy to assemble a complete STO integral package.			15. NUMBER OF PAGES	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT (U)	18. SECURITY CLASSIFICATION OF THIS PAGE (U)	19. SECURITY CLASSIFICATION OF ABSTRACT (U)	20. LIMITATION OF ABSTRACT	

GENERAL INSTRUCTIONS FOR COMPLETING SF 298

The Report Documentation Page (RDP) is used in announcing and cataloging reports. It is important that this information be consistent with the rest of the report, particularly the cover and title page. Instructions for filling in each block of the form follow. It is important to **stay within the lines** to meet **optical scanning requirements**.

Block 1. Agency Use Only (Leave blank)

Block 2. Report Date. Full publication date including day, month, and year, if available (e.g. 1 Jan 88). Must cite at least the year.

Block 3. Type of Report and Dates Covered. State whether report is interim, final, etc. If applicable, enter inclusive report dates (e.g. 10 Jun 87 - 30 Jun 88).

Block 4. Title and Subtitle. A title is taken from the part of the report that provides the most meaningful and complete information. When a report is prepared in more than one volume, repeat the primary title, add volume number, and include subtitle for the specific volume. On classified documents enter the title classification in parentheses.

Block 5. Funding Numbers. To include contract and grant numbers; may include program element number(s), project number(s), task number(s), and work unit number(s). Use the following labels:

C - Contract	PR - Project
G - Grant	TA - Task
PE - Program Element	WU - Work Unit
	Accession No.

Block 6. Author(s). Name(s) of person(s) responsible for writing the report, performing the research, or credited with the content of the report. If editor or compiler, this should follow the name(s).

Block 7. Performing Organization Name(s) and Address(es). Self-explanatory.

Block 8. Performing Organization Report Number. Enter the unique alphanumeric report number(s) assigned by the organization performing the report.

Block 9. Sponsoring/Monitoring Agency Name(s) and Address(es). Self-explanatory.

Block 10. Sponsoring/Monitoring Agency Report Number. (If known)

Block 11. Supplementary Notes. Enter information not included elsewhere such as: Prepared in cooperation with...; Trans. of...; To be published in... When a report is revised, include a statement whether the new report supersedes or supplements the older report.

Block 12a. Distribution/Availability Statement. Denotes public availability or limitations. Cite any availability to the public. Enter additional limitations or special markings in all capitals (e.g. NOFORN, REL, ITAR).

DOD - See DoDD 5230.24, "Distribution Statements on Technical Documents."

DOE - See authorities.

NASA - See Handbook NHB 2200.2.

NTIS - Leave blank.

Block 12b. Distribution Code.

DOD - Leave blank.

DOE - Enter DOE distribution categories from the Standard Distribution for Unclassified Scientific and Technical Reports.

NASA - Leave blank.

NTIS - Leave blank.

Block 13. Abstract. Include a brief (*Maximum 200 words*) factual summary of the most significant information contained in the report.

Block 14. Subject Terms. Keywords or phrases identifying major subjects in the report.

Block 15. Number of Pages. Enter the total number of pages.

Block 16. Price Code. Enter appropriate price code (*NTIS only*).

Blocks 17. - 19. Security Classifications. Self-explanatory. Enter U.S. Security Classification in accordance with U.S. Security Regulations (i.e., UNCLASSIFIED). If form contains classified information, stamp classification on the top and bottom of the page.

Block 20. Limitation of Abstract. This block must be completed to assign a limitation to the abstract. Enter either UL (unlimited) or SAR (same as report). An entry in this block is necessary if the abstract is to be limited. If blank, the abstract is assumed to be unlimited.

FINAL TECHNICAL REPORT

TITLE: "Analytical Methods Using Slater-Type Orbitals in Quantum Chemistry"

INCLUSIVE DATES: November 1, 1991 - October 31, 1995

CONTRACT/GRANT NUMBER: F 49620-92-J-0063

SENIOR RESEARCH PERSONNEL: Herbert W. Jones
Charles A. Weatherford
Babak Etemadi

PUBLICATIONS:

"Semi-Analytical Method for Four-Center Molecular Integrals Over Slater-Type Orbitals," H.W. Jones, *Int. J. Quantum Chem.* **42**, 779 (1992).

"Lowdin α -Function, Overlap Integral, and Computer Algebra," H.W. Jones, *Int. J. Quantum Chem.* **41**, 749 (1992).

"Overlap Integrals of Slater-Type Orbitals," B. Etemadi and H.W. Jones, *Boston Mathematica Conference*, 1992.

"Restricted Basis Functions for H_2^+ with Use of Overlap Integrals of Slater-Type Orbitals", H.W. Jones, B. Etemadi, and F.B. Brown, *Int. J. Quantum Chem. Symp.* **26**, 265 (1992).

"Electron Scattering From Krypton Atoms Between 1-20 eV", K.L. Baluja, A. Jain, H.W. Jones, C.A. Weatherford, and Alejandro Amaya-Tapia, *Physica Scripta* **45**, 30-34 (1992).

"Benchmark Values for Two-Center Coulomb Integrals over Slater-Type Orbital," H.W. Jones, *Int. J. Quantum Chem.* **45**, 21 (1993).

"Accurate Ground-State Calculations for H_2^+ Using Basis Sets of Atom-Centered Slater-Type Orbitals," H.W. Jones and B. Etemadi, *Phys. Rev. A* **47**, 3430 (1993).

"Accurate LCAO Ground State Calculations of HeH^{2+} Using Slater-Type Orbitals," B. Etemadi and H.W. Jones, *Int. J. Quantum Chem. Symp.* **27**, 755 (1993).

"Electron Interactions With Non-Linear Polyatomic Molecules and Their Radicals and Ions," Ashok Kumar Jain and Charles A. Weatherford, *Aero Propulsion and*

Power Directorate, Wright Laboratory, Air Force Materiel Command, Wright Patterson AFB, OH, 1993.

"Developments in Multicenter Molecular Integrals over STOs Using Expansions in Spherical Harmonics", H.W. Jones, *Int. J. Quantum Chem.* 51, 417 (1994).

"Completion of a Hybrid Theory Calculation of the P_g Resonance in Electron- N_2 scattering," C.A. Weatherford and A. Temkin, *Physical Review A* 49, 2580 (1994).

"Addition Theorem for Coulomb Sturmians in Coordinate and Momentum Space," C.A. Weatherford, in Proceedings of the 16th Annual Meeting and the 20th Day of Scientific Lectures of the National Society of Black Physicists, Florida A&M University, Tallahassee, FL (1994), edited by R.L. Williams and C.A. Weatherford.

"The (Non-Iterative) Partial Differential Equation Method: Application to Electron-Molecule Scattering," A. Temkin and C.A. Weatherford, in Computational Methods for Electron-Molecule Collisions, eds. W.M. Huo and F.A. Gianturco, Plenum, N.Y. 1995, p. 191.

"Comprehensive Strategy for The Calculation of Overlap Integrals with Slater-Type Orbitals," H.W. Jones, submitted to *Int. J. Quantum Chem.*

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

It has been our objective and that of several other groups to use Slater-type orbitals, STOs, characterized by $\exp(-R)$ in problems of ab initio quantum chemistry rather than the currently used Gaussian-type orbitals, GTOs, characterized by $\exp(-R^2)$. We believe that STOs will give more accurate results because they can fulfill a cusp condition and have correct asymptotic behavior. This was proven by us in the case of H_2^+ . But the real test would be for molecules with two or more atoms and electrons.

The general molecular problem requires at most four-center molecular integrals. In just the last year we have devised an accuracy and fast method for processing STO molecular integrals: interior regions are done by Gauss-Legendre integration after α -function expansions, and exterior regions analytically with the aid of look-up tables for the evaluation of basic integrals. C, E, and F matrices that facilitate the calculations are

Availability Codes	
Dist	Avail and/or Special
A-1	

stored in memory. All our procedures have been checked by the computer algebra program *Mathematica*, which can overcome all cancellation errors.

The fact that several groups have worked many years on the STO integral problem without achieving the goal of a complete integral package, reveals the inherent difficulty of translating analytic formulation into computer programs. The most difficult part, namely, radial integrals, has now been solved with the support of the AFOSR. Now, it remains to use this strategy to assemble a complete STO integral package.

INTRODUCTION

The problem of multicenter molecular integrals over Slater-type orbitals (STOs) is a long-standing one that has been pursued in a systematic manner since the time of Kotani, Lowdin, Colson, Bartnett, Roothaan, and Ruedenberg immediately after World War II. Silverstone, Harris, Michels, Shavitts, and Steinborn continued work on the problem through the sixties and seventies. Here, at Florida A&M University, we caused renewed interest in the problem by holding an international meeting involving 35 of the most knowledgeable scientists on Slater orbitals (exponential-type orbitals) in the summer of 1981.

Today, several groups are making efforts to bring this problem to a close: Steinborn (Germany), Rico (Spain), Guseinov (Russia), Bouferguene (France), Talman (Canada), and Tai (USA). In spite of the massive effort, a general "black box" integral subroutine has not been developed. I do believe that we at Florida A&M University have finally penetrated the mystery of this "intractable" problem. With the help of the computer algebra program *Mathematica* we can increase the precision of a number (using up to 100 or more digits) and overcome cancellation errors. The knowledge of the true value of an integral gives us insight to program in FORTRAN to achieve acceptable accuracy at high speed. Our secret is that every orbital is associated with C, E, and F matrices that are to be stored in computer memory. Also, speed is achieved by

the extensive use of look-up tables. To eliminate time-consuming multiplications, a Gauss-Legendre numerical quadrature is done for interior regions. This strategy should be transparent after reading the attached paper, "Comprehensive Strategy for the Calculation of Overlap Integrals with Slater-Type Orbitals." Now that all of the hard thinking has been done, it is just a matter of time before an integral package can be assembled.

REVIEW OF PROGRESS:

1992. Our study of STOs began in 1978 (Steinborn started in 1968). It is remarkable that so much of our early work played a significant role in our final formulation of this problem. In retrospect, it appears that this long gestation period was necessary.

During 1992 we wrote a paper on semianalytical methods for four-center molecular integrals. This paper is in the spirit of our final method. The potentials were calculated analytically and the second integral was done numerically by Simpson's rule. Now we do the interior integration by Gauss-Legendre quadrature, and the exterior regions is done entirely analytically. For large values of parameters, we introduced the T and X matrices to save computer time. For small values of parameters we use expansions in E and F matrices. In this paper only 1s orbitals were used and jmax was set to 36. Now, we have precalculated jmax values for many different orbitals.

At the meeting, "Current Trends in Computational Chemistry," Jackson, Mississippi, we presented an important paper, "Benchmarks for Two-Center Exchange Integrals." In it and in an earlier paper on "The Lowdin α -function and Overlap Integrals" we worked with the computer algebra program *Mathematica*. We showed how to easily generate exact values for the C, E, and F matrices. (This had previously been done in FORTRAN, but with great difficulty). This permitted the exact determination for overlap integrals for the first time. The advantage of *Mathematica* is that we can work at any degree of precision and thereby always overcome cancellation errors. As a matter of interest, it appears that for realistic problems only 100 digits are

needed at most. But our concern is with accuracy and speed. This requires that we use FORTRAN. However, it is always comforting and helpful in programming to work toward the true answer. The exchange integral is given by an infinite sum of term, $I = \sum_{l=0}^{\infty} I_l$. Twelve terms usually give accuracies to eight digits. *Mathematica* gives the exact value for each I_l . It may be that at a later date we have to use convergence accelerators as developed by Weniger or Bouferguene.

We used a LCAO approach with only s-orbitals to find the ground state of H_2^+ . As expected, STOs proved to be more accurate than GTOs. Again, this was the case if a basis of STOs with various angular momenta were used. Once more, this was confirmed for HeH^{2+} .

1993. The one-electron three-center integral is difficult to converge if it is evaluated at the apex of an equilateral triangle. With our new Power Macintosh we felt we had a good chance to generate a closed formula for this integral. After a heroic effort we had to abandon this hope. This cleared the atmosphere, and henceforth we were free to employ numerical methods.

The invited paper, "Developments in Multicenter Molecular Integrals," was presented in Spain. Gauss-Legendre numerical integration was selected for the interior region and a Gauss-Laguerre quadrature for the exterior region.

1994. Once more an attempt was made to obtain closed formulas, but to no avail. The Gauss-Laguerre integration proved to be impractical -- too many quadrature points were needed for orbitals with high quantum numbers.

1995. All possibilities having been tried, the final formulation appeared obvious and inevitable. Now, it was just a matter of doing it first in *Mathematica* and then in FORTRAN. The spirit of the method is presented in the appended preprint, "Comprehensive Strategy for the Calculation of Overlap Integrals with Slater-Type Orbitals." Also included is a *Mathematica* version of a program for a three-center exchange integral.

CONCLUSION:

We claim to have solved the real difficulty of performing multicenter molecular integrals over Slater-type orbitals by developing an accurate and fast method for the radial integrals. The necessary angular integrals are analytic and well-known. To complete the job of obtaining a "black box" integral package with needed extensive debugging, it would be desirable to work with another group that is committed to Slater-type orbitals. After all, many persons collaborated on Gaussian-type integrals.

Comprehensive strategy for the calculation of overlap integrals with Slater-type orbitals

Herbert W. Jones
Department of Physics
Florida A & M University
Tallahassee, Florida 32307

Abstract

A strategy is presented for the calculation of two-center overlap integrals over Slater-type orbitals. Displaced orbitals are expanded in spherical harmonics with Löwdin α -functions as coefficients. The exponentials in the α -functions are expanded leading to representation in terms of stored E and F matrices. For a given precision, the number of terms needed for each orbital for a specified harmonic, and its displacement multiplied by its screening constant, is pre-determined and stored. A survey of this data is presented. The one-dimensional integration needed for the overlap is done by Gauss-Legendre numerical integration over the interior region, and analytically over the exterior. Complete stability is achieved and excellent results obtained. Implications for all multicenter molecular integrals are apparent.

I. INTRODUCTION

Slater-type orbitals (STOs), i.e., exponential type orbitals, would be desirable for basis sets in quantum chemistry and molecular physics because they can satisfy the cusp condition at nuclei and represent long range electronic behavior [1]. However, the notorious computational difficulties of STOs have led to their virtual replacement by Gaussian-type orbitals in basis sets. Nevertheless, significant progress is being made in several quarters on this long-standing problem of computing with STOs [2].

Two-center overlap integrals over STOs are needed in semiempirical and ab initio quantum chemical calculations. There is a long history, starting with Kotani [3], Mulliken [3], and Roothaan [3], of systematic attempts to obtain accurate and fast evaluations of these simplest of multicenter molecular integrals. They were not entirely successful. Even the most recent computer codes [4, 5] must contend with restrictions on parameter values.

Overlap integrals are also used to introduce new strategies for general multicenter molecular integrals. Here, we consider both uses of the overlap problem.

One might say that all mathematical methods for solving multicenter integrals are correct; it is the finite word length of computers that is at the root of the problem of implementation. Cancellation errors, i.e., the subtraction of nearly equal numbers, are endemic to computations with

STOs. These invidious cancellation or differencing errors often make results unusable. The problem of the speed of computation must also be confronted if STOs are to be competitive with GTOs. This consideration has caused us to recommend the use of a one-dimensional Gauss-Legendre numerical quadrature for the interior region of space, i.e., between the origin and the outermost orbital center.

We have had considerable success in using the Löwdin α -function method for a limited class of STOs [6]. We must now present new details so that this method can be efficiently used with any STO. The twin goals of high speed and high accuracy have been achieved here with overlap integrals with implications for all multicenter integrals.

II. THE α -FUNCTION EXPANSION

A STO $\chi = AR^{N-1}e^{-\zeta R}Y_L^M(\Theta, \phi)$ in its local coordinate system (R, Θ, ϕ) has its origin displaced to $(0, 0, a)$ in the working coordinate system (r, θ, ϕ) . Its expansion in spherical harmonics is [7]:

$$\chi = \frac{A}{\zeta^{N-1}} \left[\frac{(2L+1)(L+M)!}{4\pi(L-M)!} \right]^{1/2} (-1)^M \sum_{\ell=M}^{\infty} \left[\frac{4\pi(\ell+M)!}{(2\ell+1)(\ell-M)!} \right]^{1/2} \times \alpha_{\ell}^{NLM}(\zeta a, \zeta r) Y_{\ell}^M(\theta, \phi) \quad (1)$$

where

$$\alpha_t^{NLM}(\zeta a, \zeta r) = \frac{(2\ell+1)(\ell-M)!}{2(\ell+M)!} \sum_{i=0}^{istop} \sum_{j=0}^{jstop} C_t^{NLM}(i, j) \times H_{ij} \cdot (\zeta a)^{i-L-\ell-1} (\zeta r)^{j-\ell-1} \quad (2)$$

and

$$H_{ij} = \begin{cases} e^{-\zeta a} [(-1)^j e^{\zeta r} - e^{-\zeta r}], & r < a \\ e^{-\zeta r} [(-1)^i e^{\zeta a} - e^{-\zeta a}], & r > a \end{cases} \quad (3)$$

The normalization constant $A = (2\zeta)^{N+\frac{1}{2}} [(2N)!]^{-\frac{1}{2}}$ and $istop = N + L + \ell - M$, and $jstop = N + \ell$. Suzuki [8] has shown that $-M$ may be included in $istop$. It is necessary when using the computer algebra program *Mathematica* [9].)

As pointed out by Bouferguene and Rinaldi [10], the elements of the C -matrix $C_t^{NLM}(i, j)$ grow explosively with higher harmonics ℓ , which usually necessitates using computer algebra with arbitrary accuracy to avoid intolerable cancellation errors. Expansion of the exponentials in the α -function leads to the E -matrix for $r < a$ and the F -matrix for $r > a$ [6, 11]. The elements of these matrices are small and not intimidating. Thus,

$$\alpha_t^{NLM} = \begin{cases} e^{-\zeta a} \sum_{j=\ell}^{jmax} \sum_{i=0}^{istop} E_t^{NLM}(i, j) \cdot (\zeta a)^{i-L-\ell-1} (\zeta r)^j & (4) \\ e^{-\zeta r} \sum_{j=0}^{jstop} \sum_{i=0}^{imax} F_t^{NLM}(i, j) \cdot (\zeta a)^i (\zeta r)^{j-\ell-1} & (5) \end{cases}$$

As a general rule, computation is faster if a double sum is reduced to a single sum. Therefore, for the sake of simplicity, too, we introduce single dimensional matrices $Y_l(j)$ and $Z_l(j)$.

$$\alpha_l^{NLM}(\zeta a, \zeta r) = \begin{cases} \sum_{j=l}^{j_{\max}} Y_l(j) \cdot (\zeta r)^j, & r < a \\ e^{-\zeta r} \sum_{j=0}^{i_{\text{stop}}} Z_l(j) \cdot (\zeta r)^{j-l-1}, & r > a \end{cases} \quad (6)$$

$$e^{-\zeta r} \sum_{j=0}^{i_{\text{stop}}} Z_l(j) \cdot (\zeta r)^{j-l-1}, \quad r > a \quad (7)$$

with

$$Y_l(j) = e^{-\zeta a} \sum_{i=0}^{i_{\text{stop}}} E_l^{NLM}(i, j) \cdot (\zeta a)^{i-L-l-1}, \quad (8)$$

and

$$Z_l(j) = \sum_{i=0}^{i_{\max}} F_l^{NLM}(j, i) \cdot (\zeta a)^i \quad (9)$$

These definitions are slightly different from the previous ones because we want to emphasize that a and r always are associated with ζ . Now, the issue is how many terms in the expansions of the exponentials are to be taken, i.e., the values of j_{\max} and i_{\max} . In previous work with 1s orbitals we simply used $j_{\max} = i_{\max} = 36$.

To cover all possible values of r in the $r < a$ case we determine the value of $jmax$ to produce an error less than one part in 10^{16} of the exact value when $r = a$. The exact value was determined by using *Mathematica* set to 70 digit accuracy using a C -matrix closed formula, for the α -function. Fortunately, the values of $Y_\ell(j)$ and also the terms that add up to $Z_\ell(j)$ decrease monotonically after a few terms, so there is no ambiguity in the results. But for some STOs with very large quantum numbers there is a slight loss in accuracy to one part in 10^{12} . This could easily be overcome by using double precision, if need be.

In Table I we take orbitals up to $N = 5$, $L = 4$, $M = 4$, $\ell = 12$, and $(\zeta a) = 16$. We note that the first non-zero value of $Y_\ell(j)$ starts at $j = \ell$ and increases in steps of two; $imax$ is always equal to or less than $jmax$; $jmax$ and $imax$ increase with (ζa) and ℓ . The different values are only mildly different from each other. Therefore, interpolation is hardly necessary; we may err on the side of caution without much of a change in $imax$ or $jmax$ and produce only a small increase in computer time. For simplicity, we could even just take $imax = jmax$. These values of $jmax$ and $imax$ are to be stored as part of the data associated with an orbital as well as its E -matrix and F -matrix.

III. OVERLAP INTEGRALS

The overlap integral between two orbitals χ' and χ is given by

$$S = \int \chi' \chi \, dv \quad (10)$$

The orbital χ' is placed at the origin and χ is placed along the z -axis at $(0, 0, a)$. Then,

$$\chi' = A' r^{N'-1} e^{-\zeta' r} Y_{L'}^{M'}(\theta, \phi) \quad \text{and}$$

$$\chi = A R^{N-1} e^{-\zeta R} Y_L^M(\Theta, \Phi).$$

Expanding χ about the origin in α -functions and performing the angular integration, the orthogonality of spherical harmonics dictates that only one term with $\ell = L'$ and $M = M'$ survives [12]. Thus

$$S = K \int_0^\infty dr \, r^{N'+1} e^{-\zeta' r} \alpha_{L'}^{NLM}(\zeta a, \zeta r) \quad (11)$$

with

$$K = \frac{(-1)^M}{\zeta^{N-1}} \left[\frac{(2\zeta')^{2N'+1} (2\zeta)^{2N+1} (2L+1)}{(2N')! (2N)! (2L'+1)} \frac{(L+M)! (L'+M)!}{(L-M)! (L'-M)!} \right]^{1/2} \quad (12)$$

The integral breaks down into two parts. The first part $S1$ is the integration from 0 to a . With an eye to future developments, we decide to use a 24-point gauss-Legendre quadrature over this interior region. We have found that the α -functions are relatively smooth and therefore numerical integrations over them is very successful. The α -function is accurately evaluated using the Y_ℓ matrix with one of the $jmax$ values. If we tried an analytical approach using the C -matrix, we would be confronted with terms of the form $\exp[-(\zeta' - \zeta)r]$. Such terms, as many investigators have discovered, are a source of instability. When one examines exchange integrals using expanded α -functions, the product of two infinite series must be considered. This problem can be avoided by resorting to a numerical quadrature.

The second part of the integration $S2$ is from a to infinity. Here analytic methods may safely be employed as all exponential terms are of the form $\exp[-(\zeta' + \zeta)r]$. Thus:

$$S2 = K \sum_{j=0}^{N+\ell} Z_\ell(j) \int_a^\infty dr e^{-(\zeta'+\zeta)r} r^{N'+j-\ell} \quad (13)$$

Each integration term can readily be turned into a sum by the formula

$$\int_a^\infty dr e^{-wr} r^n = e^{-wa} \sum_{k=0}^n \frac{n!}{(n-k)!} \frac{a^{n-k}}{w^{k+1}} \quad (14)$$

The $Z_t(j)$ matrix is determined by using the Table I value for $imax$ corresponding to the appropriate orbital, harmonic, and (ζa) value.

IV. RESULTS

The strategy described here for the evaluation of overlap integrals proved to be very efficient and accurate. All overlaps attempted are accurate to at least 10^{-12} parts, as confirmed by our computer algebra program.

Table II shows our results in calculating overlap integrals done by several authors [13]. The second line of each calculation is the exact result as determined by computer algebra [13b]. The various authors provide from 6 decimal digits to 16. Our results are impressive. We achieve machine accuracy of 16 decimal digits for (744|744) with $p = 2$, $t = 1/2$ ($\zeta' = 3$, $\zeta = 1$), without the cumbersome use of formulas [13d]. All the other of our wide-ranging overlaps give 14 or 15 decimal digits, except the last case with the highest quantum numbers (10, 0, 0|10, 9, 0) [13e]: that gives 11 decimal digits. Since table I did not include all of the $jmax$ and $imax$ values needed, some were calculated individually. Eventually, all physically acceptable orbitals will have $jmax$ and $imax$ values as data.

V. CONCLUSION

Our new procedure for overlap integrals is so straight forward and stable that we can expect to approach machine accuracy on all but unusual cases. Even here, limited use of double precision can provide 16 decimal digits for all physical orbitals.

The implications for all multicenter molecular integrals are clear: Gauss-Legendre quadrature for interior regions should be used after the α -functions are expanded and evaluated on a fixed grid. The exterior regions that will only have negative exponentials may safely be handled analytically.

An ab initio calculation on a molecule would require the reading in of E - and F -matrices for each orbital of a basis set (together with their $jmax$ and $imax$ values). Then, $Y_i(j)$ and $Z_i(j)$ would be calculated over a standard grid. Now, we would be ready to calculate all multicenter molecular integrals needed. This comprehensive approach should advance the use of STOs in molecular problems.

ACKNOWLEDGMENTS

The author wishes to acknowledge the assistance of Jawahar L. Jain in determining $jmax$ and $imax$ values. Partial support was provided by NASA (CeNNAs), the AFOSR under Contract No. F49620-92-J-0063, and by the ONR Contract N00014-95-1-0614.

References

- [1] *International Conference on ETO Multicenter Molecular Integrals*, edited by C. A. Weatherford and H. W. Jones (Reidel, Dordrecht, 1982).
- [2] E. O. Steinborn, H. H. H. Homeier, and E. J. Weniger, *Theochem* **92**, 207 (1992); J. F. Rico, R. Lopez, and G. Ramirez, *J. Chem. Phys.* **91**, 4202 (1989), I. I. Guseinov, *Phys. Rev. A* **31**, 2851 (1985); A. Bourferguene, M. Fares, and D. Rinaldi, *J. Chem. Phys.* **100**, 8156 (1994).
- [3] M. Kotani, A. Ameniya, E. Ishigura, and T. Kimura, *Tables of Molecular Integrals* (Maruzen, Tokyo, 1963); R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, *J. Chem. Phys.* **17**, 1278 (1949); C. C. J. Roothaan, *J. Chem. Phys.* **19**, 1450 (1951).
- [4] H. H. H. Homeier, E. J. Weniger, E. O. Steinborn, *Comput. Phys. Commun.* **72**, 269 (1992).
- [5] J. F. Rico, R. Lopez, M. Paniagua, and G. Ramirez, *Comput. Phys. Commun.* **64**, 329 (1991).
- [6] H. W. Jones, *Phys. Rev. A* **38**, 1065 (1988); *J. Comp. Chem.* **12**, 1217 (1991).
- [7] H. W. Jones and C. A. Weatherford, *Int. J. Quantum Chem. Symp.* **12**, 483 (1978); *Theochem* **199**, 233 (1989); H. W. Jones, *Phys. Rev. A* **30**, 1 (1984).
- [8] N. Suzuki, *J. Math Phys.* **33**, 4288 (1992).
- [9] S. Wolfram, *Mathematica: A System for Doing Mathematics by Computer* (Addison-Wesley, Reading, MA, 1988).
- [10] A. Bouferguene and D. Rinaldi, *Int. J. Quantum Chem.* **50**, 21 (1994).
- [11] H. W. Jones, B. Bussery, and C. A. Weatherford, *Int. J. Quantum Chem. Symp.* **21**, 693 (1987).
- [12] H. W. Jones, *Int. J. Quantum Chem.* **18**, 709 (1980).

- [13] (a) A. K. Bhattacharya and S. C. Dhabal, *J. Chem. Phys.* **84**, 1598 (1986);
- (b) H. W. Jones, *Int. J. Quantum Chem.* **41**, 749 (1992);
- (c) H. Tai, *Phys. Rev. A* **45**, 1454 (1992);
- (d) H. W. Jones, *Phys. Rev. A* **35**, 1923 (1987);
- (e) A. Bouferguene and D. Rinaldi, *Int. J. Quantum Chem.* **50**, 21 (1994).

Orbital	ζa	l	j_{max}	i_{max}
NLM	1	2	22	22
5 4 2		6	30	25
		12	36	30
	4	2	36	32
		6	40	35
		12	46	40
	16	2	70	60
		6	70	63
		12	72	64
5 4 3	1	3	25	21
		6	28	24
		12	36	30
	4	3	35	31
		6	40	34
		12	44	38
	16	3	67	59
		6	70	61
		12	72	64
5 4 4	1	4	24	22
		6	28	24
		12	34	30
	4	4	34	32
		6	36	34
		12	44	40
	16	4	68	60
		6	68	60
		12	70	66

Table I. The values of j_{max} and i_{max} needed for 16 decimal digit accuracy of orbital NLM corresponding to ζa (screening constant times displacement distance) and harmonic l .

a	N'	L'	M'	ζ'	N	L	M	ζ	l	j_{max}	i_{max}	Overlap
1.4	5	0	0	0.1	5	0	0	0.1	0	14	14	0.9996 3718 9410 3862 0.9996 3718 9410 3858
1.4	1	0	0	10	2	1	0	2	0	30	30	0.1174 1378 9686 6282 0.1174 1378 9686 6283
1.4	1	0	0	1.02	2	1	0	1.01	0	20	18	0.4338 5680 0488 3418 0.4338 5680 0488 3414
1.0	5	2	2	1.5	5	2	2	1.4	2	26	26	0.9389 7863 3044 9063 0.9389 7863 3044 9060
1.0	7	4	4	3	7	4	4	1	4	34	32	0.1101 1047 7764 9702 0.1101 1047 7764 9702
3.0	10	0	0	8	10	0	0	2.5	0	52	48	0.2196 8618 1056 3716 0.2196 8618 1056 3724
3.0	10	0	0	2.5	10	9	0	1	0	40	35	0.1829 9253 7777 2399 (-4) 0.1829 9253 7778 2953 (-4)

Table II. Overlap integrals between orbital $\chi'(N'L'M'\zeta')$ located at the origin and $\chi(NLM\zeta)$ located at $(0, 0, a)$. First row is present method, second row is exact by computer algebra.


```

(* July 6,1995      ENERGY OF REGION 1,2,3,4,5 ; SUM i12345      *)
(* three center exchange *)
(* see H.W.Jones, J.Comp.Chem.12,1217(1991) *)

nn=1;hh=0;mm=0;z=1.2;a=2;jmax=36;w=2*z; zeta=2*z;
g1[n_,a_]:=Which[n>=0,a^(n+1)/(n+1),n<-1,a^(n+1)/(n+1),True,Log[a]];
f1[n_,a_,b_]:=Which[n>=0,(-Exp[-b*a]/b^(n+1)*Sum[n!/(n-t)!*(a*b)^(n-t),{t,0,n}]+n!/b^(n+1)),
n<-1,
((-b)^(-n-1)*Sum[(-Exp[-b*a]*(-n-t-1)!/(-n-1)!/(-b*a)^(-n-t) + (-n-t-1)!/(-n-1)!/(-n-t)!],
{t,1,-n-1}])+(-b)^(-n-1)/(-n-1)!*(ExpIntegralEi[-b*a]-Log[Abs[b]]-EulerGamma),
True,ExpIntegralEi[-b*a]-Log[Abs[b]]-EulerGamma];
f2[n_,a_,b_]:=Which[n>=0,Exp[-a*b]/b^(n+1)*Sum[n!/(n-t)!*(b*a)^(n-t),{t,0,n}],
n<-1,
(-b)^(-n-1)*Sum[-Exp[-b*a]*(-n-t-1)!/(-n-1)!/(-b*a)^(-n-t),{t,1,-n-1}],
(-b)^(-n-1)/(-n-1)!*ExpIntegralEi[-b*a],
True,-ExpIntegralEi[-b*a]];
flgam[n_,r_,z_]:=1/z^(n+1)*Gamma[n+1,0,z*r]/N;
flgam1[n_,w_]:=flgam[n,1,w];
(* activate points and weights *)
b=Sqrt[2.]; d=2.;
npoint=8;
blim=d; alim=.001;
bma=(blim-alim)/2;
apb=(alim+blim)/2;

hmax=12;
mstop=nn+30+hmax+1;
rm=Table[-bma*zz[[i]]+apb,{i,1,npoint}];
rp=Table[bma*zz[[i]]+apb,{i,1,npoint}];
vmflgam1=Table[0,{m,1,mstop},{i,1,npoint}];
vpflgam1=Table[0,{m,1,mstop},{i,1,npoint}];
Do[ vmflgam1[[m,i]]=flgam1[m,z*rm[[i]]];
vpflgam1[[m,i]]=flgam1[m,z*rp[[i]]],
{m,1,mstop},{i,1,npoint}];

alfa[r_]:=Sum[y[[q+1]]*r^q,{q,h,30,2}]
u1[r_]:=r^(nn+1)*Sum[y[[j+1]]*r^j*flgam1[nn+j+h+1,z*r],{j,h,30,2}];

bias=2*hmax-nn+1+1;
stop=bias+4nn-1;
vf2b=Table[0,{i,1,stop}];
Do[vf2b[[i]]=f2[i-bias,a,w+zeta],{i,1,stop}];
abias=-nn+2*hmax+1+1;
astop=abias+2nn-1;
vf2a=Table[0,{t,1,astop}];
Do[ vf2a[[t]]=f2[t-abias,a,zeta],{t,1,astop}];
vf2a=vf2a/N;
vf2b=vf2b/N;

aa=Sqrt[(2*z)^(2nn+1)/(2nn)!]
```

```

Timing[exchange=0.0;
Do[
yb=Table[z^j*Exp[-z*b]*Sum[ematrrix[[h+1,i+1,j+1]]*(z*b)^(i-hh-h-1),
  {i,0,nn+hh+h-mm}],{j,0,jmax}]]//N;
yd=Table[z^j*Exp[-z*d]*Sum[ematrrix[[h+1,i+1,j+1]]*(z*d)^(i-hh-h-1),
  {i,0,nn+hh+h-mm}],{j,0,jmax}]]//N;
zb=Table[z^(j-h-1)*Sum[ematrrix[[h+1,j+1,i+1]]*(z*b)^i,
  {i,h,jmax}],{j,0,nn+h}]]//N;
zd=Table[z^(j-h-1)*Sum[ematrrix[[h+1,j+1,i+1]]*(z*d)^i,
  {i,h,jmax}],{j,0,nn+h}]]//N;
q2=Sum[yb[[j+1]]*flgam[nn+1+j+h,b,z],{j,h,jmax,2}]]//N;
C3R=Table[0,{m,0,2nn+h}];
Do[C3R[[nn+j-k+1]]=C3R[[nn+j-k+1]]+zb[[j+1]]*(nn+j)!/(nn+j-k)!/w^(k+1),
  {j,0,nn+h},{k,0,nn+j}];
q3A=Exp[-w*b]*Sum[C3R[[m+1]]*b^m,{m,0,2nn+h}]]//N;
i1=0.0;
Do[
  r=rm[[i]];
  If[r <= b,volt=r^(nn+1)*Sum[yb[[j+1]]*r^j*flgam1[nn+1+j+h,z*r],{j,h,jmax,2}],
  volt=q2/r^(h+1)+q3A/r^(h+1)-Exp[-w*r]/r^(h+1)*Sum[C3R[[m+1]]*r^m,{m,0,2nn+h}]];
  If[r <= d,aval=Sum[yd[[q+1]]*r^q,{q,h,jmax}],
  aval=Exp[-z*r]*Sum[zd[[q+1]]*r^(q-h-1),{q,0,nn+h}]];
  i1=i1+bma*ww[[i]]*r^(nn+1)*Exp[-z*r]*aval*volt;
  r=rp[[i]];
  If[r <= b,volt=r^(nn+1)*Sum[yb[[j+1]]*r^j*flgam1[nn+1+j+h,z*r],{j,h,jmax,2}],
  volt=q2/r^(h+1)+q3A/r^(h+1)-Exp[-w*r]/r^(h+1)*Sum[C3R[[m+1]]*r^m,{m,0,2nn+h}]];
  If[r <= d,aval=Sum[yd[[q+1]]*r^q,{q,h,jmax}],
  aval=Exp[-z*r]*Sum[zd[[q+1]]*r^(q-h-1),{q,0,nn+h}]];
  i1=i1+bma*ww[[i]]*r^(nn+1)*Exp[-z*r]*aval*volt;
  ,{i,1,npoint}];

(*      analytic      outside      *)
w=2.*z;
i2=q2*Sum[zd[[j+1]]*f2[nn-1-2h+j,d,w],{j,0,nn+h}]]//N;

ZC3R=Table[0,{t,0,3nn+2h}];
Do[
  t=m+j;
  ZC3R[[t+1]]=ZC3R[[t+1]]+zd[[j+1]]*C3R[[m+1]],
  {j,0,nn+h},{m,0,2nn+h}];
i3R=-Sum[ZC3R[[t+1]]*f2[nn-1-2h+t,d,4.*z],{t,0,3nn+2h}]]//N;
i3A=q3A*Sum[zd[[j+1]]*f2[nn-2h-1+j,d,2.*z],{j,0,nn+h}]]//N;
i3=i3R+i3A;
i123=aa^4/(2h+1)^2*(i1+i2+i3)*LegendreP[h,1./Sqrt[2.]];
Print[h," ",i1," ",i2," ",i3," ",i123];
exchange=exchange+i123
,{h,0,12}]; Print[exchange] ]

N[exchange,16]

0.1099365385879246

```